Electronic Supplementary Material (ESI) for Dalton Transactions.

Pillar[5]arene Based Gel from Low-Molecular-Weight Gelators for Sustained Dye Release in Water

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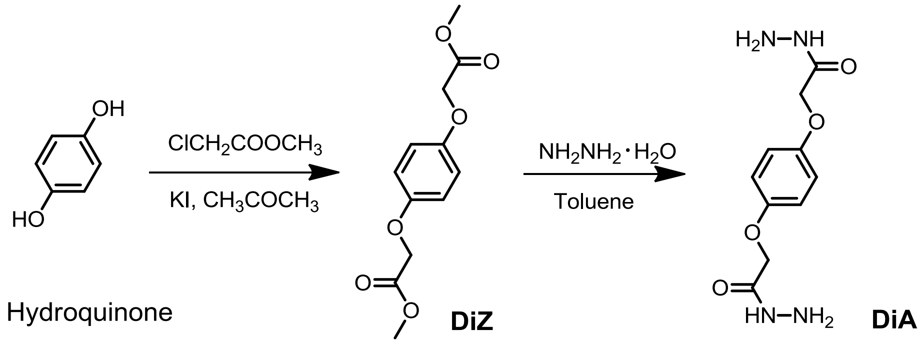
Supporting information

1. Materials and methods

Hydroquinone, methyl chloroacetate, boron trifluoride etherate, triformol, *p*-hydroxy benzaldehyde and ethane-1,2-diamine were reagent grade and used as received. **BrP5** was synthesied according the reported refference.[S1] Solvents were either employed as purchased or dried according to procedures described in the literature. ^{1}H NMR spectra were collected on a Varian Unity INOVA-400 spectrometer with internal standard TMS. ^{13}C NMR spectra were recorded on a Varian Unity INOVA-400 spectrometry at 100 MHz. Mass spectra were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with an ESI interface and an ion trap analyzer. HRMS were obtained on a Bruker 7-Tesla FT-ICRMS equipped with an electrospray source (Billerica, MA, USA). Scanning electron microscopy (SEM) investigations were carried out on a JEOL 6390LV instrument. The SEM samples were prepared on clean Si substrates. Each sample solution was deposited onto a Si substrate, placed in a refrigerator for 30 min, and freeze-dried in a freeze-drying machine at –20 ℃ under reduced pressure. Fluorescence spectra were recorded on a Hitachi F-7000 Fluorescence Spectrophotometer.

*2. Synthesis of diacylhydrazine derivative **DiA***

Scheme S1.** Synthetic route to **DiA



Anhydrous potassium carbonate (55.2 g, 400 mmol) was added to a solution of hydroquinone (44.0 g, 400 mmol) and methyl chloroacetate (216 g, 2.00 mol) in dry acetonitrile (500 mL). The mixture was stirred at 80 ℃ for 24 hours under nitrogen atmosphere. After removal of the inorganic salts by filtration, the solvent was evaporated and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate, *v*/*v* 5:1) to give **DiZ** as a white solid (76.3 g, 75%). The proton NMR spectrum of **DiZ** is shown in Figure S1. ^{1}H NMR (400 MHz, $CDCl_3$, 293K) δ (ppm): 6.84 (s, 4H), 4.57 (s, 4H), 3.78 (s, 6H). Then $NH_2NH_2 \cdot H_2O$ (67.5g, 1 mol, 80%) was added to a mixture solution (200 mL, toluene/CH_3CH_2OH = 1:1) of **DiZ** (25.4 g, 100 mmol). The mixture was stirred at 80 ℃ for 1 hour and the solvent was evaporated and the residue was purified by recrystallization in CH_3OH to give **DiA** as a white solid (24.3g, 96%). The proton NMR spectrum of **DiA** is shown in Fig. S2. ^{1}H NMR (400 MHz, DMSO-d_6, 293K) δ (ppm): 9.25 (s, 4H), 6.88 (s, 4H), 4.39 (s, 4H), 4.29 (s, 4H). The ^{13}C NMR spectrum of **DiA** is shown in Fig. S3. ^{13}C NMR (100 MHz, DMSO-d_6, 293K) δ (ppm): 167.99, 152.40, 116.04, 66.29. LR-ESI-MS is shown in Fig. S4: *m*/z 294.4 [**DiA** + K]$^+$ (100%). HR-ESI-MS: *m*/*z* calcd for [**DiA** + Na]$^+$ $C_{10}H_{14}NaN_4O_4$, 277.09; found, 277.09; error 0 ppm.

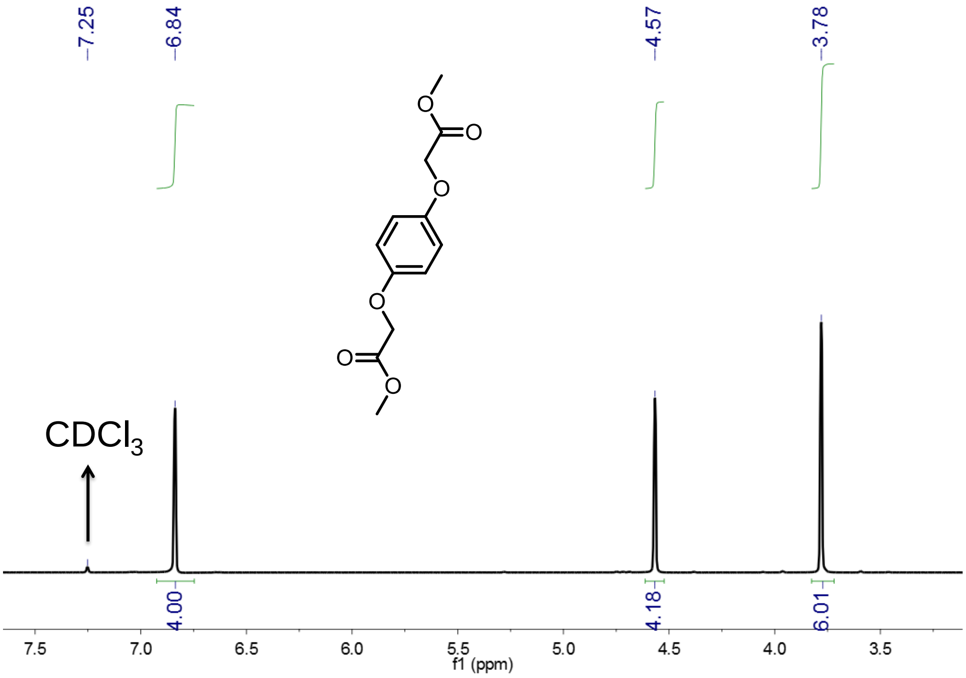


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 293 K) of monomer **DiZ**.

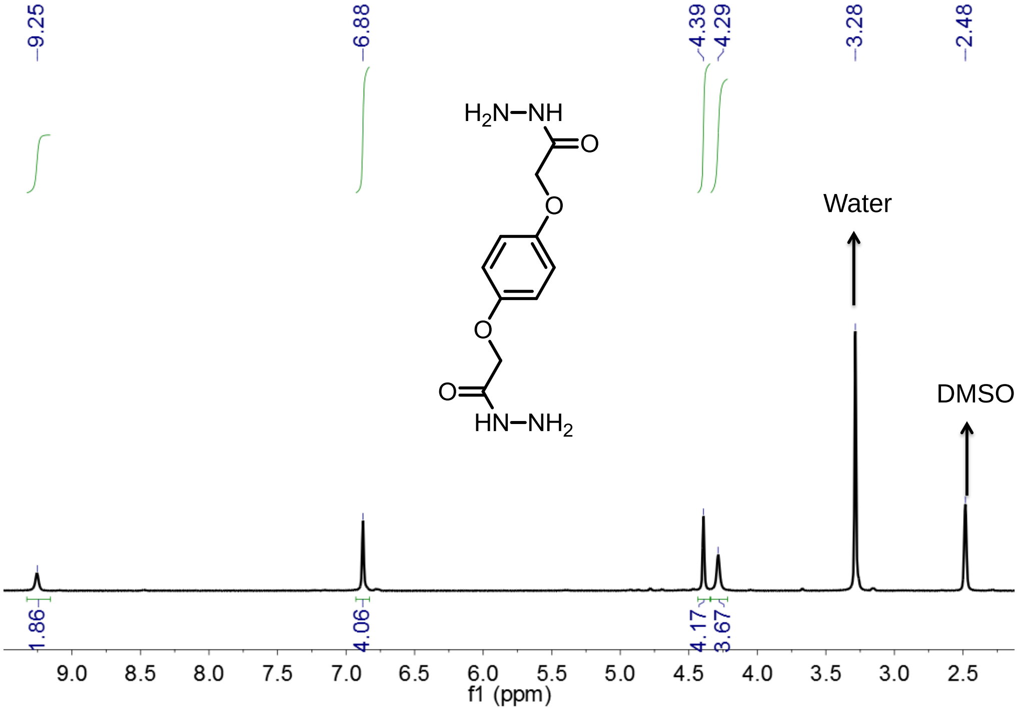


Figure S2. ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 293 K) of monomer **DiA**.

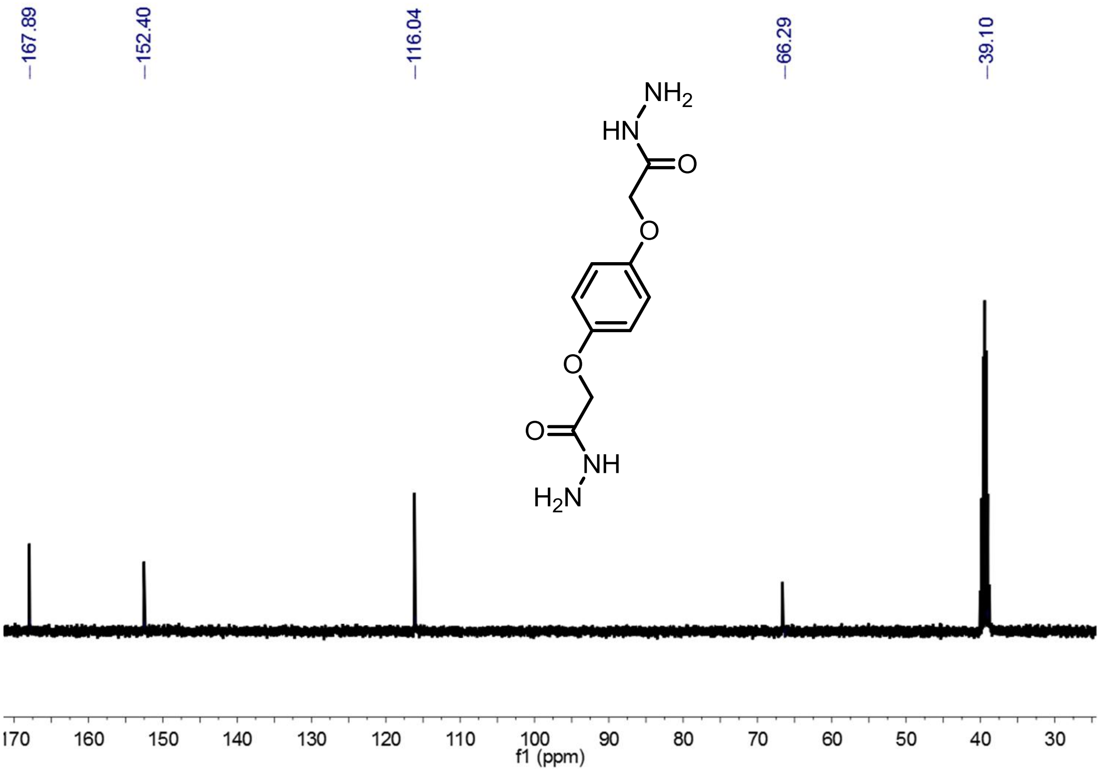


Figure S3. ^{13}C NMR spectrum (100 MHz, DMSO-d_6, 293 K) of monomer **DiA**.

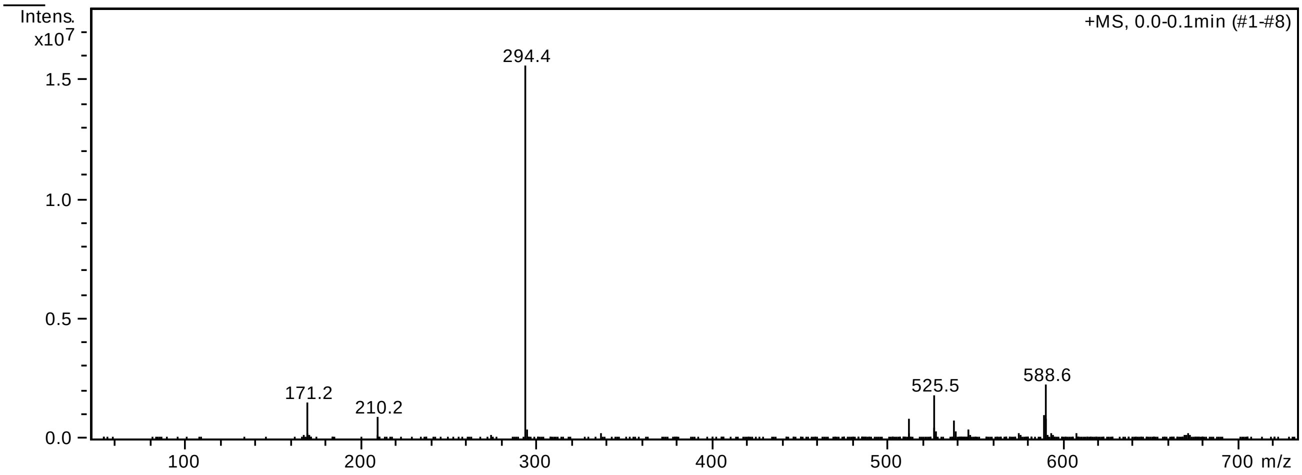
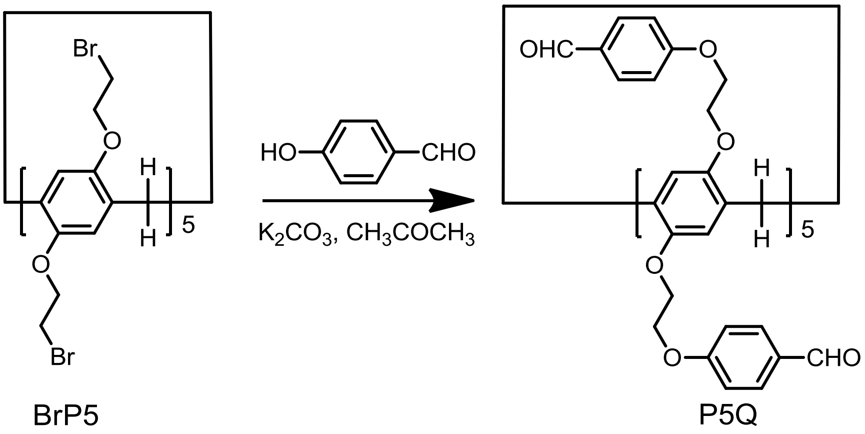


Figure S4. Electrospray ionization mass spectrum of **DiA**. Assignment of main peak: m/z 294.4 [**M** + K]$^+$ (100%).

3. Synthesis of aldehyde modified pillar[5]arene ***P5Q***

Scheme S3. *Synthetic route to* ***P5Q***



A solution of **BrP5** (16.8 g, 10.0 mmol) and *p*-hydroxybenzaldehyde (24.4 g, 200 mmol) in acetone (250 mL), then K_2CO_3 (27.6 g, 200 mmol) was added to the solution and the mixture was stirred at 80 °C for 12 hour. After removal of the inorganic salts by filtration, the solvent was evaporated and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate, *v*/*v* 10:1) to give **P5Q** as a white solid (16.9 g, 81%). The proton NMR spectrum of **P5Q** is shown in Fig. S5. ^{1}H NMR (400 MHz, chloroform-*d*, 293K) δ (ppm): 9.81 (s, 10H), 7.77 (s, 10H), 7.42-7.28 (m, 10H), 7.03-6.94 (m, 30H), 4.17 (s, 30H), 3.93-3.82 (m, 20H). The ^{13}C NMR spectrum of **P5Q** is shown in Fig. S6. ^{13}C NMR (100 MHz, chloroform-*d*, 293K) δ (ppm): 193.24, 165.33, 152.70, 132.81, 130.89, 116.58, 115.31, 67.41. LR-ESI-MS is shown in Fig. S7: *m*/z 1046.8 [**P5Q** + 2 H]$^{2+}$ (100%). ESI-TOF-MS: *m*/*z* calcd for [**P5Q** + 2Na + H_2O]$^{2+}$ $C_{125}H_{112}Na_2O_{31}$, 1057.88; found, 1057.92 (Fig. S8).

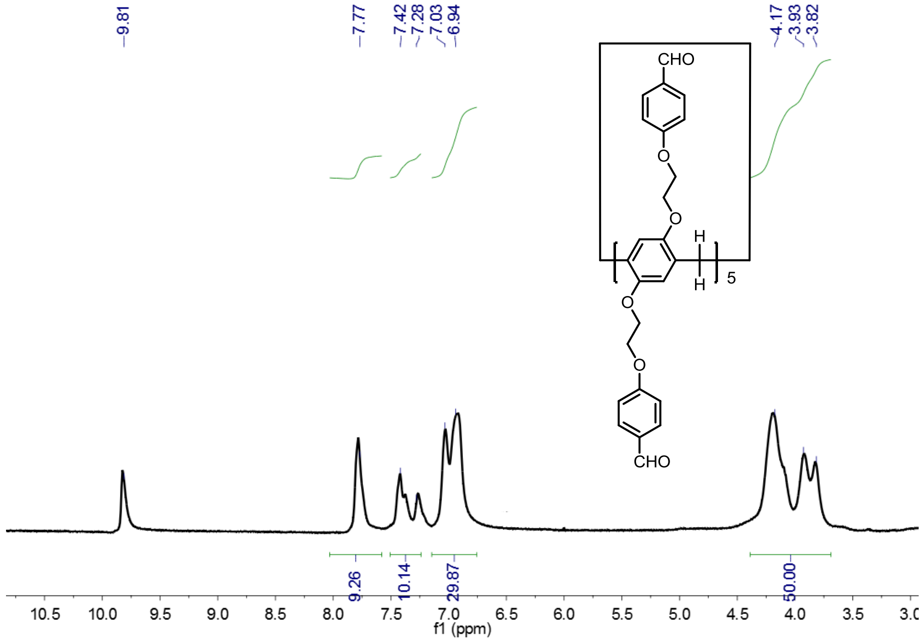


Figure S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 293 K) of **P5Q**.

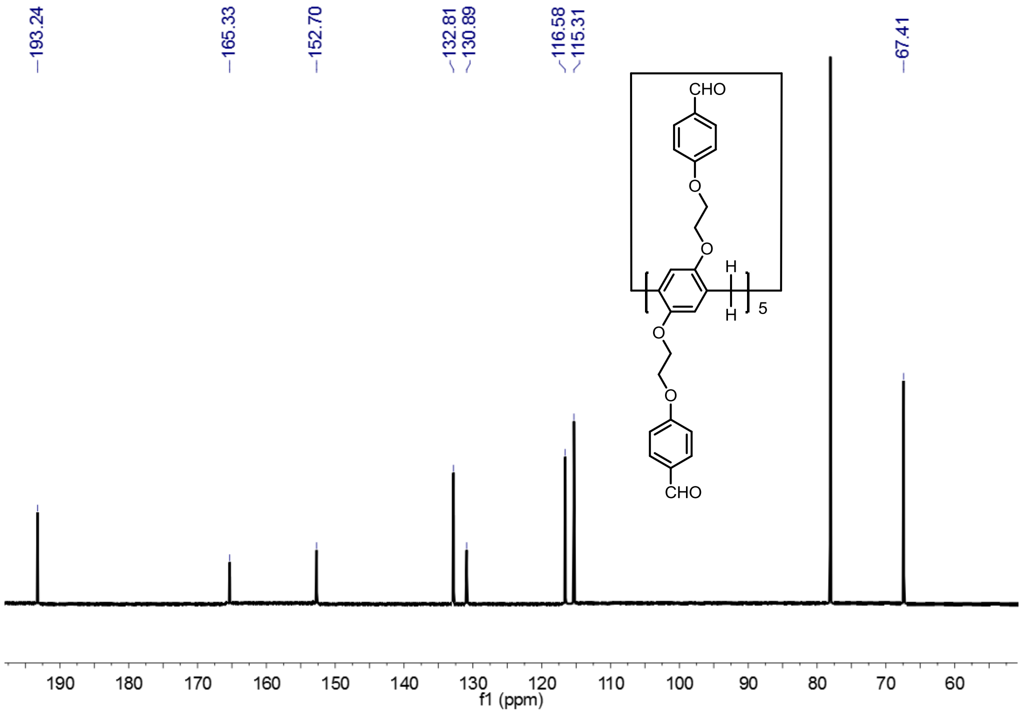


Figure S6. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 293 K) of **P5Q**.

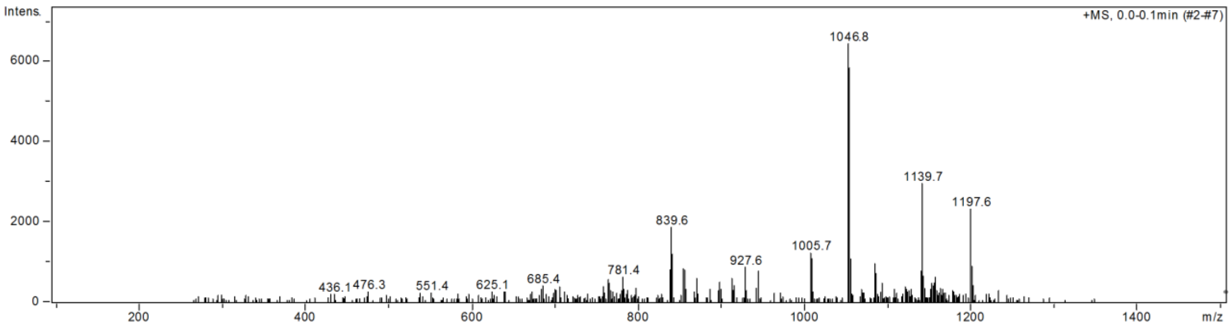


Figure S7. Electrospray ionization mass spectrum of **P5Q**. Assignment of main peak: *m*/*z* 1046.8 [**P5Q** + 2 H]$^{2+}$ (100%).

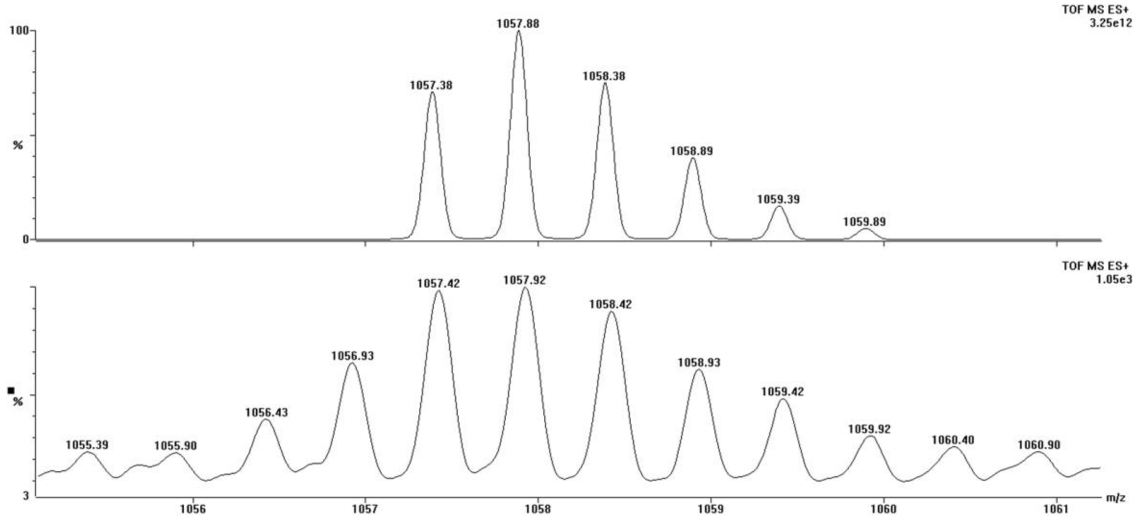


Figure S8. Experimental (down) and calculated (up) ESI-TOF-MS spectra of [**P5Q** + 2Na + H_2O]$^{2+}$.

4. *Preparation of the soft gel*

The soft gel: compound **P5Q** (41.8 mg, 0.02 mmol) and **DiA** (22.6 mg, 0.10 mmol) were dissolved in DMSO (2 mL), then a catalytic amount of HCl (0.05 mL, 1 M) was added. The gel was formed after simple stirring 1 min, and incubation at 60 °C for 1h.

The soft gel with **TPP** or **TPPE**: compound **P5Q** (41.8 mg, 0.02 mmol), **TPP** (or **TPPE** 1.00 mg) and **DiA** (22.6 mg, 0.10 mmol) were dissolved in DMSO (2 mL), then a catalytic amount of HCl (0.05 mL, 1 M) was added. The gel was formed after simple stirring 1 min, and incubation at 60 °C for 1h.

Solvent exchange: the corresponding gel with **TPP** or **TPPE** previously prepared from DMSO was immersed in H_2O (50 ml, pH = 6) at room temperature.

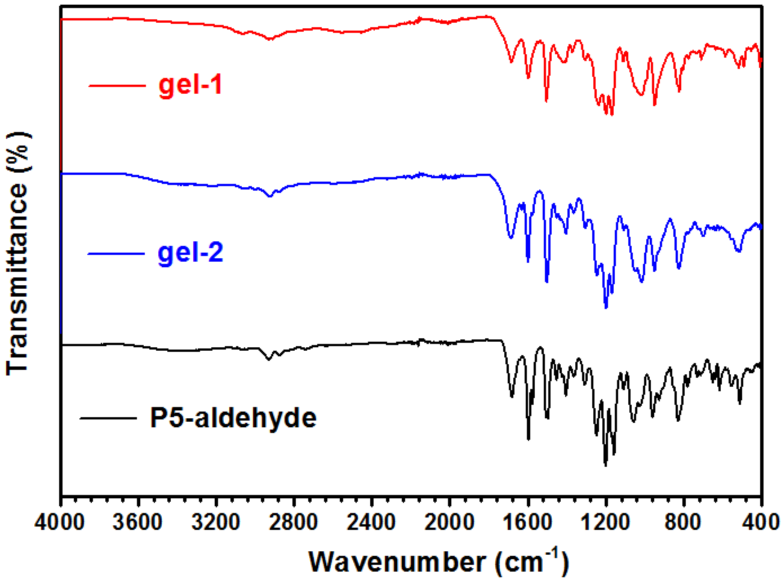


Figure S9. IR spectra of P5-aldehyde, gel-1, and gel-2. The IR spectra were obtained from freeze-dried xerogels of the respective samples indicated above. Gel-2 is the gel prepared in DMSO, and gel-1 is after solvent change in water.

5. *Stability of this supramolecular gel in different solvents*

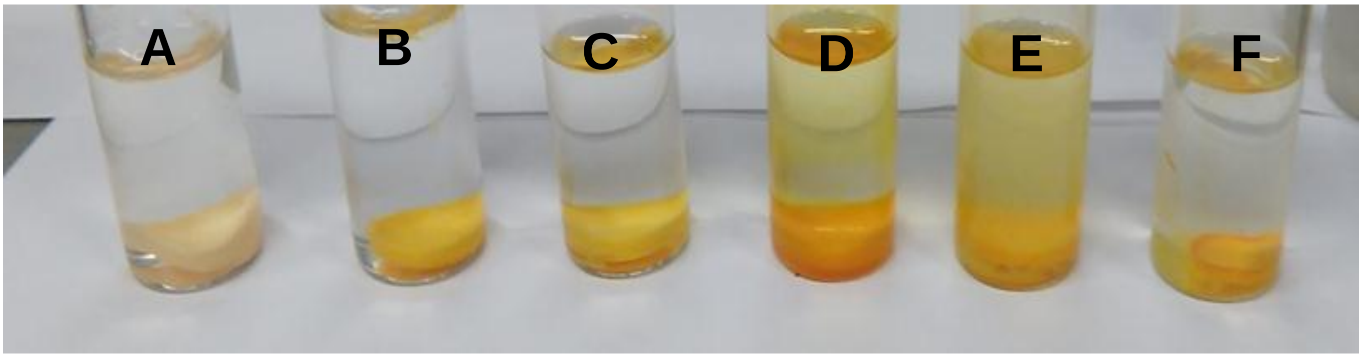


Figure S10. Optical pictures of supramolecuar gel in different solvents for 2 months: A, water (pH = 14); B, water (pH = 1); C, acetone; D, hexane; E, dichloromethane; F, ethyl acetate.

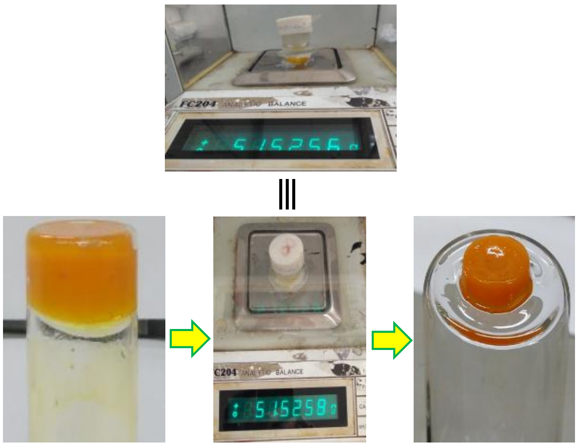


Figure S11. A cylinder-like supramolecular gel can maintain its shape after being pressed by a 50 g weight for 1 h. When we put the gel on the electronic scale, we used some grease to fix it.

Figure S12. The photographic of using laser to irradiate the solution after solvent exchange. We can see very weak Tyndall Effect.

6. References

S1. a) Y. Ma, X. Ji, F. Xiang, X. Chi, C. Han, J. He, Z. Abliz, W. Chen, F. Huang, *Chem. Commun.*, **2011**, *47*, 12340; b) Y. Yao, J. Li, J. Dai, X. Chi, M. Xue, *RSC Adv.* **2014**, *4*, 9039.